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A Theoretical Treatment of the Absorption and Emission Properties of Cu(II) Porphyrin

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Introduction:

Cu(II) porphyrins (Cu(II)P), figure 1, have been studied extensively both experimentally and theoretically[1-9]. Among the interesting spectroscopic features of these complexes, a luminescence quenching has been observed when chelating in the fifth position with pyridine (*pyr*) and other σ-donor ligands[1-3]. This effect has been attributed to the presence of low-energy states that can be either of the d-d or charge transfer (CT) type[4]. Controversy exists also in the literature regarding the assignment of this mediating state as being of d-π* or π-d character. Several models have been proposed to explain the nature of this state[4-9] but none of these has been entirely successful in interpreting the spectroscopy of these complexes.

It is the aim of this work to examine the luminescence quenching observed in these systems through electronic structure calculations on Cu(II)P and Cu(II)P:*pyr* complexes. We use for these studies methods based on SCF/CI as described below, in contrast to methods based on molecular orbital (*mo*) or MS X_α schemes[5-9]. As shown further such an approach is highly successful in reproducing the spectroscopy of Cu porphyrins. It is therefore expected to correctly interpret the origin of the corresponding states of these complexes.

Calculations:

The calculations are performed within the Intermediate Neglect of Differential Overlap model parametrized directly on electronic spectroscopy, INDO/S[10,11]. A self-consistent field (SCF) calculation is performed using the restricted open-shell formalism, ROHF[12]. This calculation is then followed by a configuration interaction calculation (CI) that includes some 1045 singly excited configurations (CIS) for Cu(II)P and some 1126 singly excited configurations for the Cu(II)P-pyridine complex. A valence-bond, or Rumer Diagram, construction is used for this purpose[13,14]. This is essentially all single excitations from orbital 37 to 82 in the former case, where *mo* number 62 is the singly occupied Cu d(x^2-y^2) *mo*, and from orbital 41 to 97, in the latter case, where 77 is the singly occupied *mo*. Three separate calculations have been done on the Cu(II)P-pyridine complex, one in which the Cu to pyridine nitrogen

distance is 2.2 Å, a second in which this distance was set to 2.0 Å and a third in which this distance was set to 1.8 Å. Although the last distance may seem too short to be reasonably obtained, we wanted to examine this extreme asymptote. All calculations were done using the ZINDO program package[15].

Results and Discussion:

The molecular orbital diagram we obtain for the Cu(II)P complex is shown in Figure 2. The labeling is *(mo. no., symmetry)*. The mapping of the symmetry labels with these symmetry numbers is given in Table 1. The symmetry labels are given for the subgroup D_{2h} in which the calculation was performed. This is the largest subgroup of the actual symmetry of this complex, D_{4h}. The orbital labeled (62,1) is principally Cu-$d(x^2-y^2)$, is of symmetry b_{1g} in D_{4h} (a_g in D_{2h}), and is singly occupied. The orbital (61,2) is the highest energy occupied, and is of $a_{1u}(\pi)$ symmetry in D_{4h} (a_u in D_{2h}). The next highest occupied *mo* is (60,4), $a_{2u}(\pi)$ in D_{4h} (b_{1u} in D_{2h}). The lowest unoccupied *mo*'s are a degenerate pair (63,3) and (64,5), $e_g(\pi^*)$ in D_{4h} (b_{2g} and b_{3g} in D_{2h}). Note that the singly occupied $d(x^2-y^2)$ *mo* is not the HOMO, as is often the case in SCF calculations involving d localized *mo*'s. As relaxation is very large for such orbitals, nothing should be inferred from the location of this orbital about electron affinities or ionization processes that measure the energy differences between *states*. Removal of an electron from (61,2) and placing it in (62,1) corresponds to a ligand to metal charge transfer excitation and is at considerably higher energy than the state represented in figure 2, see later.

Porphyrin spectra are usually described, at least qualitatively, within the four orbital model of Gouterman[16]. Promotion of an electron from the frontier $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals into the $e_g(\pi^*)$ lead to two close lying $E_{1u}(\pi\text{->}\pi^*)$ states with considerable calculated oscillator strength. These two states then interact, leading to a lower lying Q band in which the oscillator strengths tend to cancel, and a higher lying state, the B or Soret, in which the transition moments reinforce. These states are reported in Table 2

as Q and B. The discussion of Q within the four orbital model is reasonably accurate while that of B is only partially complete. Other singly excited states mix with the B band complicating its description, as do higher excitations (double and triple excitations). For these reasons the energy of the Q band is usually calculated in good agreement with experiment, and the B band is calculated some 3,000-4,000 cm^{-1} too high in energy, and with too high an oscillator strength. That is also the case here. The Q band maximum for Cu(II)OEP (octaethyl porphyrin) is reported at 17,670 cm^{-1} in the vapor, to be compared with a calculated value of 15,926 cm^{-1}, while the B band is reported at 25,810 cm^{-1}, 2,700 cm^{-1} lower than our calculated value[17].

As the Cu(II) ion of this complex is a doublet, the overall spin multiplicity of the ground state of the complex is also doublet. The normal singlet manifold of the porphyrin macrocycle is also doublet. The porphyrin triplets also interact with the Cu(II) doublet forming doublets (the trip-doublets of the tables) and quartets (trip-quartets) from the usual rules of the addition of angular momentum[18,19]. The quartet components of these triplet states are calculated at 8,531 cm^{-1} and 13,367 cm^{-1} representing an exchange splitting of 393 cm^{-1} and 530 cm^{-1} respectively.

Ake and Gouterman report emmision in Cu(II)TPP (tetraphenyl porphyrin) at 13,300 cm^{-1} which they attribute to the trip-quartet[19], in excellent agreement with our *second* trip-quartet. Although we have found excellent metal-ligand and metal-metal exchange splittings in a variety of systems, CIS calculations of the type performed here using the INDO model have often produced ligand triplet states too low in energy compared to their singlet counterparts, the latter of which are generally in good accord with experiment[20]. It may be that our porphyrin triplets are calculated too low in energy, and thus all states derived from them, trip-doublets and trip-quartets, would also be calculated too low. If it is the *first* trip-quartet that Ake and Gouterman observe, the error in calculated energy for this state would be about 5000 cm^{-1}, a value which seems rather large for the INDO/S model.

In addition to the usual Q and B bands of the porphyrin macrocycle and the trip

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doublets that are now spin allowed transitions, there are d->d LaPorte transitions and ligand-to-metal and metal-to-ligand charge transfer transitions. As shown in Table 1 these are all calculated at energies higher than the allowed Q band, and would be difficult to detect as they have no appreciable oscillator strength. The first transitions with predicted oscillator strength are ^2A_g -> ^2E_u calculated at 24,572 cm^{-1}, and these would be buried under the B band. The absorption of this complex should be 'normal', while phosphorescence via the trip-doublets might compete with the fluorescence[19].

Cu(II) porphyrin complexes with strong field fifth position ligands do not emit[2]. This by itself suggest the presence of a new state below the Q band that is populated via internal conversion from the Q band, and then to the ground state. Likely candidates for this new state are charge transfer from the Cu(II)P moiety to the fifth position ligand, now tightly bound, or bands that have considerable Cu-d(z^2) orbital participation, as the position of the doubly occupied d(z^2) *mo* should be highly dependent on the presence of fifth and sixth position ligands.

Tables 2 and 3 report the results of calculations on Cu(II)P-pyridine complexes at two different geometries, both with C2v symmetry. At the 2.2 Å geometry a transition to a state of $^2A_1$ symmetry that is over 50% d(z^2)->d(x^2-y^2) is calculated just below the Q band. This state is of the same symmetry as is the ground state in C2v, and efficient internal conversion might be expected. At 2.2 Å this transition has been predicted red shifted by over 6,000 cm^{-1} from its position in the Cu(II)P complex. At the 2.0 Å geometry, Table 3, this transition is further red shifted by 3,000 cm^{-1}. We note that the calculation with Cu(II)-pyridine distance of 1.8 Å yielded this transition at 7,930 cm^{-1}, below both calculated trip-doublets. In all cases this transition is predicted to have considerable ligand-to-metal charge transfer character (a2u(π)->d(x^2-y^2)), a mixing made possible through the reduction in symmetry from D4h to C2v. We attribute the absence of the normal emission to the presence of this state.

Our calculated spectra are presented as figure 3. We note the reproduction in these

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calculations of the observed red shift of both Q and B band upon stronger chelation in the fifth position[4]. We also calculate a larger red shift for the B band than for the Q band, also in accord with observed trends[4].

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Table 1: Cu(II) Porphyrin reference state ^2A_g in D2h. Irreducible representations are: $1=^2A_g$, $2=^2A_u$, $3=^2B_{1g}$, $4=^2B_{1u}$, $5=^2B_{2g}$, $6=^2B_{2u}$, $7=^2B_{3u}$ and $8=^2B_{3g}$.

	ENERGY(CM-1)	(NM)	OSC. STR.	SYM	No. IN IRREP	Comments
1	0.0	0.0	0.0000	1	1	
2	8923.7	1120.6	0.0000	7	2	trip-doub
3	8923.7	1120.6	0.0000	6	2	trip-doub
4	13893.0	719.8	0.0000	7	3	trip-doub
5	13893.1	719.8	0.0000	6	3	trip-doub
6	15926.3	627.9	0.0640	6	4	Q band
7	15926.4	627.9	0.0640	7	4	Q band
8	18390.2	543.8	0.0000	8	2	d(x2-y2) - eg(pi*)
9	18390.2	543.8	0.0000	5	2	d(x2-y2) - eg(pi*)
10	19489.4	513.1	0.0000	2	2	a1u(pi)-d(x2-y2)
11	20281.4	493.1	0.0000	3	2	(pi)- (pi*) mixed
12	21544.8	464.1	0.0000	1	2	d(z2)-d(x2-y2)
13	21668.0	461.5	0.0000	4	2	a2u(pi)-d(x2-y2)
14	22261.3	449.2	0.0000	1	3	a1u(pi)- a1u(pi*)
15	22958.1	435.6	0.0000	5	3	d(xz)-eg(pi*)
16	22958.2	435.6	0.0000	8	3	d(yz)-eg(pi*)
17	23269.6	429.7	0.0000	3	3	(pi)-(pi*) mixed
18	24226.3	412.8	0.0000	3	4	(pi)-(pi*) mixed
19	24571.6	407.0	0.0015	6	5	
20	24571.7	407.0	0.0015	7	5	
21	26002.9	384.6	0.0000	3	5	d(xy)-d(x2-y2)
22	26194.2	381.8	0.0000	1	4	
23	27504.5	363.6	0.0000	3	6	
24	28566.2	350.1	2.2494	6	6	B band
25	28566.3	350.1	2.2495	7	6	B band

Table 2: Cu(II)Porphyrin + 2.2Å pyridine in C2V symmetry. Irreducible representations are labelled 1 = $^2A_1$, 2 = $^2A_2$, 3 = $^2B_1$ and 4 = $^2B_2$

	ENERGY(CM-1)	(NM)	OSC. STR.	SYM	No. IN IRREP	COMMENTS
1	0.0	0.0	0.0000	1	1	
2	8477.9	1179.5	0.0000	4	2	trip-doub
3	8531.4	1172.1	0.0000	3	2	trip-doub
4	13007.6	768.8	0.0000	4	3	trip-doub
5	13042.9	766.7	0.0000	3	3	trip-doub
6	15229.7	656.6	0.0000	1	2	50%d(z2)-d(x2-y2)
7	15465.2	646.6	0.0445	3	4	Q
8	15530.9	643.9	0.0426	4	4	Q
9	17006.2	588.0	0.0000	4	5	d(x2-y2) - eg(pi*)
10	17041.0	586.8	0.0000	3	5	d(x2-y2) - eg(pi*)
11	19368.1	516.3	0.0000	2	2	pi-pi*
12	19652.9	508.8	0.0000	3	6	d(xz)-d(x2-y2)
13	20855.3	479.5	0.0000	2	3	d(xy)-d(x2-y2)
14	21130.3	473.3	0.0001	4	6	d(yz)-d(x2-y2)
15	21308.7	469.3	0.0000	1	3	pyridine pi-pi*
16	21917.8	456.3	0.0000	1	4	pi-pi*
17	22107.7	452.3	0.0000	2	4	pi-pi*
18	22806.1	438.5	0.0017	4	7	pi-pi*
19	22855.8	437.5	0.0018	3	7	pi-d(x2-y2)
20	22973.3	435.3	0.0000	2	5	a1u(pi)-d(x2-y2)
21	23273.6	429.7	0.0000	2	6	pi-pi*
22	24171.4	413.7	0.0000	1	5	a2u(pi)-d(x2-y2)
23	25047.5	399.2	0.0000	1	6	pi-pi*
24	26760.6	373.7	0.0104	3	8	a1u(pi)-pyr(pi*)
25	26800.0	373.1	0.0000	2	7	pi-pi*
26	26830.0	372.7	0.0115	3	9	a1u(pi)-pyr(pi*)
27	27363.1	365.5	1.7434	3	10	B
28	27423.2	364.7	1.6762	4	8	B

Table 3: Cu porphyrin + pyridine at 2.0Å in C2v Symmetry. See table 2 for symmetry labels.

	ENERGY(CM-1)	(NM)	OSC. STR.	SYM	No. IN IRREP	COMMENTS
1	0.0	0.0	0.0000	1	1	
2	8395.7	1191.1	0.0000	4	2	trip-doub
3	8460.3	1182.0	0.0000	3	2	trip-doub
4	12233.5	817.4	0.0000	1	2	a2u(pi)-d(x2-y2) + d(z2)-d(x2-y2)
5	12781.7	782.4	0.0000	4	3	trip-doub
6	12802.2	781.1	0.0000	3	3	trip-doub
7	15305.7	653.4	0.0372	3	4	Q
8	15370.3	650.6	0.0340	4	4	Q
9	17092.3	585.1	0.0000	4	5	d(x2-y2) -eg(pi*)
10	17120.7	584.1	0.0000	3	5	d(x2-y2) -eg(pi*)
11	19223.3	520.2	0.0000	2	2	pi-pi*
12	19491.7	513.0	0.0000	3	6	d(xz)-d(x2-y2)
13	20845.9	479.7	0.0000	2	3	d(xy)-d(x2-y2)
14	21277.3	470.0	0.0002	4	6	d(yz)-d(x2-y2)
15	21287.3	469.8	0.0000	1	3	pyridine pi-pi*
16	21874.0	457.2	0.0000	1	4	pi-pi*
17	21899.2	456.6	0.0000	2	4	pi-pi*
18	22397.2	446.5	0.0030	4	7	pi-pi*
19	22433.5	445.8	0.0032	3	7	pi-pi*
20	22904.9	436.6	0.0000	2	5	a1u(pi)-d(x2-y2)
21	22994.7	434.9	0.0000	2	6	pi-pi*
22	23987.9	416.9	0.0000	1	5	a2u(pi)-d(x2-y2)
23	24733.6	404.3	0.0000	1	6	pi-pi*
24	26207.1	381.6	0.6429	4	8	split B (35%a2u(pi)->pyr-pi*)
25	26219.6	381.4	0.0850	3	8	
26	26268.1	380.7	0.0893	3	9	
27	26576.5	376.3	1.2947	3	10	B
28	26665.0	375.0	0.0000	2	7	
29	26900.0	371.7	0.7846	4	9	split B (35%a2u(pi)->pyr-pi*)

Figure Captions:

Figure 1: The Cu(II) Porphyrin - pyridine complex of this study, Cu(II)P:*pyr* .

Figure 2.The frontier molecular orbitals of Cu(II)P. *mo*'s with orbital energies ±0.05 Hartrees (1 Hartree = 27.21 eV) are plotted as degenerate. The notation (N M) refers to N= *mo* number and M=*mo* symmetry. The assignment of the symmetry numbers to irreducible representations is given in the heading to Table 1. Note that *mo* (62,1) is half-filled. It is not the highest occupied *mo* due to the large amount of relaxation energy associated with doubly occupying this orbital. The excitation (61 2) -> (62 1) is a charge transfer excitation and lies at higher energy than the configuration designated by this picture, see text.

Figure 3. The simulated spectra of Cu(II)P——, Cu(II)P:*pyr* at 2.2 Å ···· and Cu(II):*pyr* at 2.0 Å ---. The vertical lines with no widths shown refer to forbidden excitations. The first taller line at about 8000 cm^{-1} is the mixed (CT d->d) state in Cu(II)P:*pyr* at 1.8 Å, the shorter four lines mark the location of the trip-doublets, which do not change much upon pyridine chelation. The next taller line is the (CT d->d) transition at about 12,500 cm^{-1} in Cu(II)P:*pyr* at 2.0 Å, and the line at 15,500 cm^{-1} the (CT d->d) transition in Cu(II)P:*pyr* at 2.2 Å
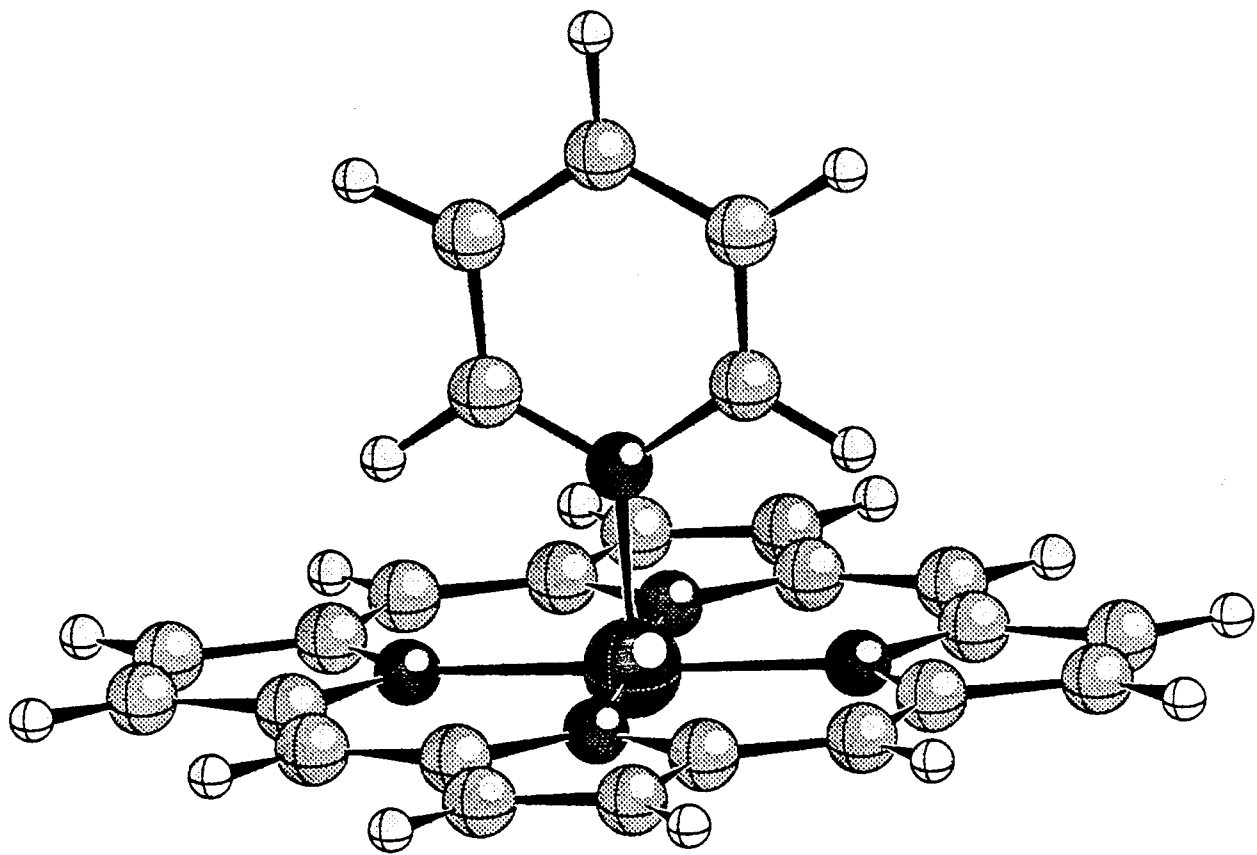
Figure 1

0.10	(73,8)	—	P(π^*)
0.09	(70,4) (71,1) (72,5)	— — —	P(π^*) S P(π^*)
0.07	(67,5) (68,8) (69,2)	— — —	P(π^*) P(π^*) P(π^*)
0.04	(66,4)	—	P(π^*)
0.01	(65,2)	—	P(π^*)
-0.05	(63,5) (64,8)	— —	P(π^*) P(π^*)
-0.24	(61,2)	↑↓	P(π)
-0.26	(60,4)	↑↓	P(π)
-0.33	(58,5) (59,8)	↑↓ ↑↓	P(π) P(π)
-0.34	(57,4) (62,1)	↑↓ ↑	P(π) Cu d(x2-y2)
-0.35	(54,8) (55,5) (56,4)	↑↓ ↑↓ ↑↓	P(π) P(π) P(π)
-0.41	(53,2)	↑↓	P(π)
	(49,3) (50,1) (51,7) (52,6)	↑↓ ↑↓ ↑↓ ↑↓	Cu d(z2) P(σ) P(σ) P(σ)
-0.46	(48,1)	↑↓	P(σ)
-0.47	(45,5) (46,8) (47,3)	↑↓ ↑↓ ↑↓	Cu d(yz) Cu d(xy)
-0.48	(43,7) (44,6)	↑↓ ↑↓	P(σ) P(σ)
-0.52	(41,1) (42,4)	↑↓ ↑↓	P(σ) P(π)

Figure 2

Figure 3